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Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt19

Synthesis of tris(Cyclohexylisocyanide)bis(Triph Perchlorate. An Example of Unusual Stabilization of the Cobalt(II) Oxidation State.

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To cite this article: Clifford A. L. Becker (1997) Synthesis of tris(Cyclohexylisocyanide)bis(Triphenylphosphine)Cobalt(II) Perchlorate. An Example of Unusual Stabilization of the Cobalt(II) Oxidation State., Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 27:10, 1527-1542, DOI: 10.1080/00945719708003157

To link to this article: http://dx.doi.org/10.1080/00945719708003157

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SYNTHESIS OF *TRIS*(CYCLOHEXYLISOCYANIDE)*BIS*(TRIPHENYL-PHOSPHINE)COBALT(II) PERCHLORATE. AN EXAMPLE OF UNUSUAL STABILIZATION OF THE COBALT(II) OXIDATION STATE.

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ABSTRACT

A cobalt(II) complex with alkylisocyanide and triarylphosphine ligands is reported. *Tris*(cyclohexylisocyanide)*bis*(triphenylphosphine)cobalt(II) perchlorate, $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$, was synthesized by PPh₃ ligand-substitution in $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$, in which the distribution of product among $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$, $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$, $[Co(OPPh_3)_4](ClO_4)_2$, and unreacted $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ was controlled in part by the concentration of PPh₃ and reaction time. $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ was also synthesized by AgClO₄ oxidation of $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$. $[Co(CNC_6H_{11})_3$. $(PPh_3)_2](ClO_4)_2$ is easily reduced to $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ with N₂H₄.H₂O and decomposes into $[Co(OPPh_3)_4](ClO_4)_2$ on prolonged dissolution in CH₂Cl₂ solution, especially under UV (365 nm) irradiation. Physical properties for $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ and $[Co(OPPh_3)_4](ClO_4)_2$ support trigonal bipyramidal and tetrahedral solution and solid state stereochemistries, respectively, but both complexes have limited stability in most solvents.

INTRODUCTION

Reaction of triarylphosphines with cobalt(II)-organoisocyanide complexes has b e e n characterized by reduction/ligand-substitution. *Pentakis*(arylisocyanide)cobalt(II) complexes, $[Co(CNR)_5]X_2.nH_2O, X = ClO_4, BF_4$, reacted with excess triarylphosphine produce disubstituted Co(I) complexes, $[Co(CNR)_3(PR_3)_2]X$, in good yields¹⁻⁷. Reactions of $[Co(CNCMe_3)_4H_2O](ClO_4)_2^{8,9}$ and $[Co_2(CNCHMe_2)_{10}](ClO_4)_4.5H_2O^{1,10}$ with excess triarylphosphine also produce the corresponding disubstituted Co(I) complexes in good yields. In only one instance, a Co(II) complex, $[Co(CNCHMe_2)_3{P(C_6H_4OMe-p)_3}_2](ClO_4)_2$, has been recovered, and this is as a minor product and under restricted reaction conditions¹¹. Reduction, as well as ligand substitution, then, is characteristic of triarylphosphine reactions with Co(II)-organoisocyanide complexes.

The availability of the triarylarsine-alkylisocyanide cobalt(II) complexes, $[Co(CNR)_4(AsR_3)_2]X_2$, $CNR = CNC_6H_{11}$, CNC_4H_9 -*n*, $CNCHMe_2$, $CNCH_2Ph$, AsR_3 $= AsPh_3$, $As(C_6H_4Me$ -*p*)_3, Ph₂AsCH₂CH₂AsPh₂, $X = ClO_4$, BF_4^{12} , now offers a possible indirect route for synthesizing cobalt(II) complexes with both organoisocyanide and triarylphosphine ligands. Phosphorus ligands can often displace coordinated arsine ligands¹³, so attempting to substitute the triarylarsines with triarylphosphines before Co(II) reduction occurs, seems a reasonable reaction to attempt. What is rather surprising in this reaction is the general formula of the Co(II) complex isolated: $[Co(CNR)_3(PPh_3)_2](ClO_4)_2$ rather than $[Co(CNR)_4(PPh_3)_2](ClO_4)_2$, and the relatively high stability of Co(II) in the presence of the one mole of liberated alkylisocyanide.

RESULTS AND DISCUSSION

Tris(cyclohexylisocyanide)bis(triphenylphosphine)cobalt(II) perchlorate, $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2, was synthesized by two different reactions. The reaction of [Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2 with excess PPh_3 produces both$ $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2 and [Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4, as shown in eq (1).$

$$[\operatorname{Co}(\operatorname{CNC}_{6}\operatorname{H}_{11})_{4}(\operatorname{AsPh}_{3})_{2}](\operatorname{ClO}_{4})_{2} \xrightarrow{\operatorname{excess PPh}_{3}} [\operatorname{Co}(\operatorname{CNC}_{6}\operatorname{H}_{11})_{3}(\operatorname{PPh}_{3})_{2}](\operatorname{ClO}_{4})_{2}} (1)$$

The relative amounts are dependent in part upon reaction conditions. A small excess of PPh₃ (1:2.5 Co:P mole ratio, or lower) and/or shorter reaction time favor production of $[Co(CNC_6H_{11})_3(PPh_3)_2](CIO_4)_2$, with some unreacted $[Co(CNC_6H_{11})_4$. (AsPh₃)₂](CIO₄)₂ starting material remaining. Greater concentrations of PPh₃ (1:3.5 Co:P mole ratio, or higher) and/or longer reaction time increase the production of $[Co(CNC_6H_{11})_3(PPh_3)_2](CIO_4)_2$, the relatively small amounts of Co(II) complex remaining unreduced being easily reduced with hydrazine [eq (2)].

$$[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2 \xrightarrow{N_2H_4} [Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$$
(2)

Reaction of $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ with a slight molar excess of AgClQ produces $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ also, however [eq (3)].

$$[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4 \longrightarrow [Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2 \qquad (3)$$

Thus mutual interconversion of $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ and $[Co(CNC_6H_{11})_3-(PPh_3)_2]ClO_4$ has been achieved, eq (4).

$$[\operatorname{Co}(\operatorname{CNC}_{6}\operatorname{H}_{11})_{3}(\operatorname{PPh}_{3})_{2}](\operatorname{ClO}_{4})_{2} \xrightarrow{\operatorname{N}_{2}\operatorname{H}_{4}} [\operatorname{Co}(\operatorname{CNC}_{6}\operatorname{H}_{11})_{3}(\operatorname{PPh}_{3})_{2}]\operatorname{ClO}_{4}$$
(4)
AgClO₄

If $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ is allowed to remain in CH_2Cl_2 solution for a prolonged period, especially under UV (365 nm) irradiation, it is converted to $[Co(OPPh_3)_4](ClO_4)_2$, eq (5).

$$hv$$

$$2[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2 \longrightarrow [Co(OPPh_3)_4](ClO_4)_2$$
(5)

Characterization of $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ in the solid state includes the following properties. Melting range: 195-200°C (dec.). IR, v(N=C): 2190 vs, 2208 w(sh), ~2155 vw(sh) cm⁻¹ (Nujol); see Fig. 1. Magnetic susceptibility: $\chi_g = 850 \pm 18 \times 10^{-9}$ (cgs), $\mu_{eff} = 1.92 \pm 0.01$ BM. Diffuse reflectance electronic spectrum: $\lambda_{max} \approx 920$ br (A = 1.4), ~670 (0.50), ~470 (1.5), ~330 br (2.4) nm. In solution: IR, v(N=C): 2188 vs cm⁻¹ (CF₃CH₂OH); 2192 vs, 2105 vw, 2076 vw cm⁻¹ (CH₂Cl₂); 2190 vs, 2098 m, 2073 m cm⁻¹ (CH₃NO₂); see Fig. 1. Molar conductivity: 290 (CH₃CN), 235 (acetone), 210 (CH₃OH), 165 (CH₃NO₂), 34 (CH₂Cl₂) Ω^{-1} cm²mol⁻¹. Electronic spectra: 932 br (175), 463 (780), ~356 (12,500), 329 (13,500), ~282 sh (13,000), ~273 sh (13,500), 229.5 sh (44,500) nm (CF₃CH₂OH); 928 br (195), 455 (925), ~351 (9,750), 327 (10,500), ~ 265 br (22,000) nm (CH₂Cl₂).

Physical properties for $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ have been reported in ref. [14]. Characterization of $[Co(OPPh_3)_4](ClO_4)_2$ in the solid state includes the following properties. Melting range: 305-320°C (dec.). IR, v(P=O): 1161 m, 1141 s, 1120 m(sh) cm⁻¹ (Nujol). Magnetic susceptibility: $\chi_g = 8.00 \pm 0.25 \times 10^{-6}$ (cgs), $\mu_{eff} = 5.28 \pm 0.08$ BM. Diffuse reflectance electronic spectrum: 632 (0.55), 604 (0.58), 588 (0.56), 563 sh (0.49), ~554 sh (0.46), ~477 sh (0.20), 462 (0.21), ≈295 sh (0.26), 274 (1.8), ~265 (1.8) nm. In solution: electronic spectra: ~1775 (39), ≈1620 (41), ~1400 (39), 637 (370), 606 (325), 586 (285), 562 (230), ~552 sh (215), 272 (8400), 265 (10,100), 259 (7500), ~255 sh (5400) nm (CF_3CH_2OH); 1760 (21), ~1540 (23), ~1400 (24), 637 (150), 606 (145), 585 (140), 563 (125), ~553 sh (120), 272.5 (8700), 266 (10,400), 260 (8,000), ~255 sh (5600) nm (CH_2Cl_2, decomposing). Molar conductivity: 165 (CH_3NO_2), 16 (CH_2Cl_2, decomposing) Ω⁻¹ cm² mol⁻¹; samples rapidly decompose in CH₃CN, acetone, and CH₃OH.

Synthesis of the Complexes

Ligand substitution reaction in $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ with excess PPh₃ to produce $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ in good yield presents two rather



Fig. 1. The v(N=C) IR Pattern for $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ in Nujol (top) and in CH_2Cl_2 (bottom).

interesting observations: the general formula for the product is [Co(CNR)₃- $(PR_3)_2$ (ClO₄)₂, not [Co(CNR)₄(PPh₃)₂](ClO₄)₂, and not all of the Co(II) has been reduced to Co(I). The six-coordinate Co(II) species, [Co(CNC₆H₁₁)₄(PPh₃)₂](ClO₄)₂, has been isolated, however, as minor product, in rapid reaction of $[Co(CNC_6H_{11})_5]$ - $(ClO_4)_2$ in EtOH with PPh₃¹⁵. The less soluble $[Co(CNC_6H_{11})_4(PPh_3)_2](ClO_4)_2$ precipitated immediately, while the major product of [Co(CNC₆H₁₁)₃(PPh₃)₂]ClO₄ remained in solution and required addition of ether for precipitation. Upon attempted recrystallization of [Co(CNC₆H₁₁)₄(PPh₃)₂](ClO₄)₂, from CH₂Cl₂/ether, however, only the five-coordinate Co(II) complex, [Co(CNC₆H₁₁)₃(PPh₃)₂](ClO₄)₂, was isolated in poor yield, the remainder of the Co(II) being reduced to Co(I)¹⁵. Thus, $[Co(CNC_6H_{11})_4(PPh_3)_2](ClO_4)_2$ may be initially formed in the reaction with $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ as well, but dissociates into $[Co(CNC_6H_{11})_3(PPh_3)_2]$ - $(ClO_4)_2$ before it can be isolated. The only difference between ligand substitution reactions with PPh₃ and AsPh₃ in these Co(II)-alkylisocyanide systems would then be the relative stabilities of the six-coordinate Co(II) species, $[Co(CNC_6H_{11})_4(AsPh_3)_2]^{2+1}$ being stable enough to be isolated and [Co(CNC₆H₁₁)₄(PPh₃)₂]²⁺ dissociating into $[Co(CNC_{4}H_{11})_{3}(PPh_{3})_{2}]^{2+}$. Reactions with PPh₃ and AsPh₃ should be analogous.

That all of the $[Co(CNC_6H_{11})_3(PPh_3)_2]^{2+}$ formed doesn't reduce into $[Co(CNC_6H_{11})_3(PPh_3)_2]^+$ in the presence of the liberated CNC_6H_{11} may be due, at least in part, to the presence of the free AsPh₃. The ability of AsPh₃ and SbPh₃, but not PPh₃, to apparently *deactivate* RNC (alkyl and aryl) has been recognized¹⁶, but not satisfactorily explained¹⁷. IR and electronic spectra give no evidence of chemical reaction between RNC and AsPh₃¹⁷, yet RNC does not seem to show the usual reactions when in the presence of free AsPh₃. Here, also, more of the Co(II) complex could be expected to have been reduced in the presence of the presumably free CNC_6H_{11} .

Increased reaction time and increased PPh₃:Co(II) mole ratio were seen to favor $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ formation over $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$. Longer reaction time should allow more Co(II) to be reduced by the CNC_6H_{11} released in the reaction, but why greater concentration of PPh₃ should increase Co(II) reduction is

unclear. Reduction of $[Co(CNCHMe_2)_3{P(C_6H_4OMe_P)_3}_2](ClO_4)_2$ was seen to proceed rapidly upon introduction of free RNC, but did not take place for addition of excess PR₃¹¹. More PPh₃ may simply make the ligand substitution take place more rapidly and thereby go further to completion, since with 2.5:1 PPh₃:Co(II) mole ratio substantial amounts of unreacted $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ were observed.

With 3.0:1 PPh₃:Co(II) mole ratio, however, an even lower yield of $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ was obtained, and for mole ratios of 3.5:1 and above, $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ was the major product. $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ was still observed, as minor product, for a mole ratio of 4.0:1. Reduction of $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ to $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ with hydrazine is an easily anticipated reaction, since *pentakis*(organoisocyanide)cobalt(II) complexes are reduced to *pentakis*(organoisocyanide)cobalt(I) with hydrazine¹⁸. When N₂H₄.H₂O was added in the initial reaction, the yield of $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ was increased to 65% (crude), 62% (recrystallized).

Oxidation of $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ to $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ with AgClO₄ may open a new synthetic route for the preparation of Co(II) complexes prone to reduction in ligand substitution reactions. Now the mutual interconversion of $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ and $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ has been achieved. Larger excess of AgClO₄ caused lower yields, possibly through Ag⁺ oxidation and/or complexation of CNC_6H_{11} . Since $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ slowly decomposes in CH_2Cl_2 solution, but is stable in CF_3CH_2OH , CF_3CH_2OH was initially used as the solvent for the AgClO₄ oxidation reaction. The yield was substantially lower (48% vs. 64%), however, probably due to the difficulty in crystallizing the product from CF_3CH_2OH /ether. The oxidation of $[Co(CNR)_3(PR_3)_2]$ - ClO_4 to $[Co(CNR)_3(PR_3)_2](ClO_4)_2$ using AgClO₄ may be contrasted with the reduction of $Co(CNR)_4I_2$ to $[Co(CNR)_5]I$ using Ag^{18} , underscoring just how sensitive these oxidation/reduction reactions are to relatively slight modifications of the complex and/or reaction conditions.

Decomposition of $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ in solution follows several different patterns. Dilute solutions in CH₃CN and acetone decompose fairly

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rapidly (*i.e.*, one day) into colorless solutions (possibly very pale pink) that may be indicative of solvent coordinated Co(II) species. The complex appears to be indefinitely stable in CF₃CH₂OH, however, with only slight decrease in the ϵ values after 3-4 months. In CH₂Cl₂ and CH₃NO₂ decomposition into blue solutions could be easily recognized as formation of the tetrahedral complex [Co(OPPh₃)₄]-(ClO₄)₂. This solution decomposition is apparently less general than that of [Co(CNC₆H₁₁)₄(AsPh₃)₂](ClO₄)₂, into [Co(OAsPh₃)₄](ClO₄)₂, which takes place in acetone, CH₃CN, and CF₃CH₂OH as well as in CH₂Cl₂ and CH₃NO₂¹⁹. Reaction under UV (365 nm) irradiation is faster for [Co(CNC₆H₁₁)₃(PPh₃)₂](ClO₄)₂ (50 h) than for [Co(CNC₆H₁₁)₄(AsPh₃)₂](ClO₄)₂ (85 h), although the overall yield is lower (54% vs. 76%, respectively)¹⁹. Otherwise, these two solution decomposition reactions appear to be very analogous. [Co(OPPh₃)₄](ClO₄)₂ has of course been previously reported²⁰, but was synthesized from excess OPPh₃ and Co(ClO₄)₂.6H₂O in ethanol, not from solution decomposition of a Co(II)-PPh₃ complex.

What is also significant about these reactions is how easily reduction or oxidation can take place. $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ readily reduces to $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ in the assumed presence of free CNC_6H_{11} , yet oxidation of PPh₃, at least, to OPPh₃, takes place in the same solvent, again in the assumed presence of free CNC_6H_{11} when sufficient time is allowed. Triarylarsine complexes, by contrast, show no tendency for Co(II) reduction in the synthesis of $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2^{12}$, but are analogously prone to oxidation of AsR₃ to OAsR₃ in preparation of the $[Co(OAsR_3)_4]X_2$ complexes (R = Ph, C_6H_4Me-p , $X = ClO_4$, $BF_4)^{19}$, and even show spontaneous Co(II) oxidation in the formation of $[Co(CNC_4Ph_4)_4(OAs(C_6H_4Me-p)_3)_2](BF_4)_3^{21}$. The synthesis of $[Co(CNC_6H_{11})_3, (PPh_3)_2](ClO_4)_2$ thus appears to be a stabilization of cobalt in a somewhat precarious oxidation state.

Characterization of the Complexes

The physical properties of $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ are compatible with an axially disubstituted trigonal bipyramidal structure in solution and a slightly distorted

trigonal bipyramidal structure in the solid state (see Fig. 2). The properties of the effective magnetic moment, v(N=C) IR pattern, and reflectance and solution electronic spectra are all analogous to those for $[Co(CNCHMe_2)_3 \{P(C_6H_4Me_p)_2]$ $(ClO_4)_{2}^{11}$, whose properties were interpreted as indicating trigonal bipyramidal structure. The solution (*i.e.* CF₃CH₂OH) v(N=C) pattern of a single strong band is appropriate for a D_{3h} axially disubstituted trigonal bipyramid. The additional weak shoulder in the Nujol IR probably indicates slight distortion from idealized geometry in the solid state. The 2084-2087 (br) cm⁻¹ band seen in CH₂Cl₂ and CH₃NO₂ solution is undoubtedly due to the intense absorption for Co(I) species, probably a small concentration of $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ formed by slight reduction in these solvents. Molar conductivity values (Λ_{M}) indicate 2:1 electrolyte behavior²². Solution and diffuse reflectance electronic spectra are equivalent over the range observed. indicating that the coordination does not change substantially upon dissolution. This spectrum is appropriate for trigonal bipyramidal coordination. The effective magnetic moment (μ_{eff}) of 1.92 BM is effectively within the range observed for lowspin Co(II) complexes, 2.0-2.7 BM23, again expected for trigonal bipyramidal coordination. The diamagnetic susceptibility for the CNC₆H₁₁ ligand was measured¹² as $\chi_g = -637 \pm 8 \times 10^{-9}$, $\chi_M = -69.5 \pm 0.9 \times 10^{-6}$ cgs.

In the crystallization/recrystallization of $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ from concentrated CH₂Cl₂ solution, sometimes a rust-brown microcrystalline product was obtained, which converted to the characteristic golden-yellow product overnight with 6.7% loss of weight. This weight loss probably indicates a molecule of CH₂Cl₂ (7.1% by mass), initially adducted in the crystal and then lost to the atmosphere with a breakdown of well-formed crystals. A similar behavior was observed with the $[Co(CNCHMe_2)_3\{P(C_6H_4OMe-p)_3\}_2](ClO_4)_2$ complex¹¹, and is indeed typical for organoisocyanide-Co(I) complexes^{24,25}. A v(N=C) frequency of 2193 vs cm⁻¹ (Nujol) and a pattern (2193 vs, 2216 w(sh), ~2153 vw(sh) cm⁻¹) analogous to that for the golden-yellow form suggests that little or no actual change in bonding has taken place.

 $[Co(OPPh_3)_4](ClO_4)_2$ was initially concluded to be tetrahedral on the basis of magnetic and spectral data²⁰, and the physical properties reported here are similar to



Fig. 2. Trigonal Bipyramidal Structure for [Co(CNC₆H₁₁)₃(PPh₃)₂](ClO₄)₂.

those previously published^{20,26,27}. Solution electronic spectra are visually very similar²⁷, and this is the distinctive pattern customarily observed for tetrahedral Co(II) complexes. The room temperature Curie's law effective magnetic moment of 5.28 \pm 0.08 BM is somewhat higher than the more accurately measured Curie-Weiss law value of 4.72 BM, with $\theta = -5.5^{\circ 20}$, but is still unambiguously indicative of three-electron paramagnetism. The actual difference in these two values of the μ_{eff} is not as great as it appears to be. A similar case was observed with [Co(OAsPh₃)₄](ClO₄)₂. Room temperature measurements, necessarily fit to Curie's law, were in good agreement: 4.79 BM¹⁹ *vs.* 4.73 BM²⁸, but when measurements made over a temperature range were fit to the Curie-Weiss law, and correction for temperature independent paramagnetism was included²⁹, the μ_{eff} decreased to 4.55 BM. The \pm 0.08 BM is the standard deviation (σ) in three measurements on the same sample, an estimation of the precision, not necessarily the accuracy, of these measurements. The v(P=O) IR frequencies are shifted to lower frequency relative to the free ligand (*i.e.* 1193 cm^{-1 30}), as would be expected.

EXPERIMENTAL

The $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ complex was synthesized from commercially available CNC_6H_{11} (Strem Chemicals, Inc., Newburyport, MA 01950, USA) as

previously reported¹². Anhydrous diethyl ether was filtered through an alumina column immediately before use. IR spectra were recorded on a Perkin Elmer 2000 FT-IR and a Mattson Polaris FT-IR. Solution electronic spectra were recorded on a Shimadzu UV-365 spectrometer; diffuse reflectance spectra were measured with an integrating sphere over the range 860-240 nm. Magnetic susceptibility was measured at room temperature using a Johnson Matthey magnetic susceptibility balance. The effective magnetic moment was calculated assuming Curie's law behavior. Molar conductivities were measured on ~0.001 M solutions at 25°C using a Crison Model 525 conductimeter. The C, H, and N elemental analyses were performed using a Carlo Erba CHN-O/S Elemental Analyzer, Model 1106. Microsamples were weighed on a Sartorius ultramicro electrobalance.

The complexes prepared are perchlorate salts, and as such must be considered as potentially explosive. These particular complexes, however, have shown no explosive tendency, even upon measurement of the melting/decomposition ranges; i.e. decomposition into dark-colored tars is gradual and nonviolent. Of all the perchlorate salts of Co(I), Co(II), and Co(III)-organoisocyanide complexes synthesized in the Laboratory over a thirty year span, only [Co(CNC₆H₄Me₂-2,6)₅](ClO₄)₂ 0.5H₂O and $[Co(CNC_{6}H_{3}Me_{2}-2,6)_{4}(ClO_{4})_{2}]$ have shown violent decomposition upon measurement of their melting/decomposition ranges, and this was short of a bona fide explosion¹⁶. Justification for using ClO_4 , instead of BF₄, is simply that perchlorate salts of Co(II)alkylisocyanide complexes (for CNR = CNC_6H_{11} , $CNCMe_3$, $CNCHMe_2$, and CNC_4H_9 *n*) crystallize better than tetrafluoroborate salts. (For $CNR = CNCH_2Ph$, however, BF₄ salts crystallize better than ClO₄ salts.) Some normal precautions for handling perchlorate solutions are already dictated by the chemistry of the organoisocyanide ligands: free RNC decompose in strong acid or upon heating. Reactions are performed on a small scale, and solid state IR spectra are measured in Nujol mull (not KBr wafer), with samples ground in Nujol (never dry).

Synthesis of [Co(CNC₆H₁₁)₃(PPh₃)₂](ClO₄)₂

A 500 mg (0.382 mmol) sample of $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ was dissolved in 3.5 mL of CH₂Cl₂, filtered through cotton using 0.5 mL of CH₂Cl₂ rinse, and chilled in ice. Then 251 mg (0.957 mmol) of PPh₃ (1:2.5 Co:P mole ratio) dissolved in 1.0 mL of CH₂Cl₂ was added dropwise with stirring. The yellow-green solution became dark yellow-brown upon addition of the ligand, but the odor of free CNC₆H₁₁ was not detected. After ligand addition was completed, ether was added dropwise. Initial precipitation, as whitish streaks on the walls of the flask, was observed after addition of 10.0 mL of ether. A total of 20.0 mL of ether was added, and the reaction mixture was chilled in ice for 45 min. The golden yellow solid was filtered from the pale orange filtrate and washed twice with 2.0 mL portions of ether. The crude product (305 mg, 72% yield) was dissolved in 2.5 mL of CH₂Cl₂, filtered through cotton, and precipitated by dropwise addition of 5.0 mL of ether. After thorough chilling in ice (1 h), the golden-yellow microcrystals were filtered from a pale yellow-green solution and washed twice with 2.0 mL portions of ether. Yield: 246 mg (81% recovery; 58% overall yield); m. pt. 195-200°C (dec.). *Anal.* Calc. for CoC₅₇H₆₃Cl₂N₃O₈P₂ [fw = 1109.87 g/mol]: C, 61.69; H, 5.72; N, 3.79. Found: C, 61.64; H, 5.73; N, 3.54%.

Another 10.0 mL of ether was added dropwise to the initial filtrate, and the resulting cloudy orange solution was refrigerated overnight. Mixed dark green and golden yellow solids were filtered from a golden yellow filtrate and washed twice with ether (73 mg; 14-17% yield). The IR spectrum for the mixed solid confirmed the presence of $[Co(CNC_6H_{11})_4(AsPh_3)_2](CIO_4)_2$ (dark green, $v(N \equiv C) = 2211 \text{ cm}^{-1}$) as well as $[Co(CNC_6H_{11})_3(PPh_3)_2](CIO_4)_2$ (golden yellow, $v(N \equiv C) = 2190 \text{ vs cm}^{-1}$), and the absence of $[Co(CNC_6H_{11})_3(PPh_3)_2]CIO_4$ (golden yellow to orange). Partial evaporation of the solvent (overnight) produced a small crop (33 mg) of mixed blue and green solids. The $v(N \equiv C)$ frequency confirmed the presence of $[Co(CNC_6H_{11})_4(AsPh_3)_2](CIO_4)_2$. The blue solid is probably $[Co(OAsPh_3)_4](CIO_4)_2$, $[Co(OPPh_3)_4](CIO_4)_2$, or a mixture of these two tetrahedral species.

Synthesis of [Co(CNC₆H₁₁)₃(PPh₃)₂]ClO₄

A 500 mg (0.382 mmol) sample of $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ was dissolved in 4.0 mL (total) of CH₂Cl₂, filtered through cotton, and chilled in ice. Then 351 mg (1.34 mmol) of PPh₃ (1:3.5 Co:P mole ratio) dissolved in 1.0 mL of CH₂Cl₂ was added dropwise with stirring. The yellow-green solution became red-orange in color upon addition of the PPh₃, but the odor of free CNC_6H_{11} was not detected. When the ligand addition was completed, ether was added dropwise. The initial precipitation commenced after addition of 20.0 mL of ether. A total of 40.0 mL of ether was added, and the reaction mixture was chilled in ice for 1.5 h. The golden yellow to pale orange solid (227 mg) was filtered from the dark orange filtrate and washed twice with 2.0 mL portions of ether. The filtrate was allowed to evaporate overnight to a dark orange gelatinous oil, which was redissolved in 2.0 mL of CH_2Cl_2 .

Dropwise addition of 4.0 mL of ether and chilling in ice (1 h) afforded a small second crop (8 mg).

The crude product was dissolved in 1.0 mL of CH_2Cl_2 and treated with 3 drops of N_2H_4 , H_2O . The heterogeneous reaction mixture was stirred vigorously for 1.5 min, after which the CH_2Cl_2 solution was carefully decanted and filtered through cotton. The residual aqueous phase was rinsed twice with 0.5 mL portions of CH_2Cl_2 , which were filtered through cotton and combined with the initial aliquot. Dropwise addition of 10.0 mL of ether induced precipitation. A total volume of 20.0 mL of ether was added, and the mixture was chilled in ice for 30 min. The light orange solid was filtered and washed twice with 2.0 mL portions of ether. Yield: 196 mg (83% recovery; 51% overall yield); m. pt. 165-180°C (dec.). Anal. Calc. for $CoC_{57}H_{63}Cl-N_3O_4P_2$ [fw = 1010.42 g/mol]: C, 67.76; H, 6.28; N, 4.16. Found: C, 67.31; H, 6.21; N, 4.20%.

Alternate Synthesis of [Co(CNC₆H₁₁)₃(PPh₃)₂](ClO₄)₂

A 400 mg (0.396 mmol) sample of $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ was dissolved in 1.5 mL of CH_2Cl_2 and filtered through cotton using an additional 0.5 mL of CH_2Cl_2 as rinse. Then 90 mg (0.434 mmol) of crushed AgClO₄ (1:1.10 Co:Ag mole ratio) was added, and the heterogeneous reaction mixture was stirred vigorously for 5.0 min. The white AgClO₄ turned black upon contact with the solution, and an Ag mirror eventually formed on the walls of the flask. The solution was decanted from the residual solid and filtered through cotton two times, with a 0.5 mL CH₂Cl₂ rinse each time, giving a total volume of 3.0 mL. Ether was added dropwise to the clear, dark yellow-brown solution. Initial precipitation was observed after addition of 2.5 mL of ether. A total of 5.0 mL of ether was added, and the reaction mixture was chilled in ice for 45 min. The golden yellow product (290 mg) was filtered from the dark yellow filtrate and washed twice with 2.0 mL portions of ether. A small second crop (36 mg) was obtained by addition of 15.0 mL of ether to the filtrate and thorough chilling in ice (1 h). The crude product (326 mg; 74% yield) was dissolved in 2.0 mL of CH₂Cl₂, filtered through cotton, and precipitated by dropwise addition of 5.0 mL of ether. After chilling in ice (45 min), the golden-yellow solid was filtered from the pale yellow filtrate and washed twice with 2.0 mL portions of ether. Yield: 280 mg (86% recovery; 64% overall yield); m. pt. 195-200°C (dec.). *Anal.* Calc. for CoC₅₇H₆₃Cl₂N₃O₈P₂ [fw = 1109.87 g/mol]: C, 61.69; H, 5.72; N, 3.79. Found: C, 61.70; H, 5.74; N, 3.76%.

Synthesis of [Co(OPPh₃)₄](ClO₄)₂

A 500 mg (0.451 mmol) sample of $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ was dissolved in 5.0 mL of CH₂Cl₂, filtered through cotton, and irradiated under a 365 nm light source for 50 h. During this time interval, the color of the solution changed from initial dark yellow-brown, through yellow-green, dark green, and dark blue, to dark blue-purple, with the slight precipitation of colorless crystals. The solution was filtered through cotton, then ether was added dropwise. Initial precipitation commenced after addition of 3.5 mL of ether; a total volume of 8.0 mL of ether was added, and the solution was chilled in ice for 1 h. The dark blue solid was filtered from the pale blue liquid and washed two times with 1.5 mL portions of ether. Overnight partial evaporation and addition of more ether to the filtrate resulted in the formation of a dark blue oil, which was eventually discarded. The crude product (218 mg, 71% yield) was dissolved in 3.5 mL of CH₂Cl₂, filtered through cotton, and precipitated by dropwise addition of 3.5 mL of ether. After chilling in ice for 45 min, the dark blue solid was filtered and washed two times with 1.5 mL portions of ether. Yield: 167 mg (77% recovery; 54% overall yield); m. pt. 305-320°C (dec,). Anal. Calc. for $CoC_{72}H_{60}Cl_2O_{12}P_4$ [fw = 1370.96 g/mol]: C, 63.08; H, 4.41; (N, 0.00). Found: C, 63.05; H, 4.57; (N, 0.03%).

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Received:	19 February 1997	Referee I:	T. Burkey
Accepted:	19 August 1997	Referee II:	K. M. DeArmond